(21) International Application Number:

RLD INTELLECTUAL PROPERTY ORGANIZAT International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6: F01N 3/00, 3/310, F02D 23/00, B01D

(11) International Publication Number: A1

WO 95/27128

49/00, 53/92, 53/94, C01B 21/20

(43) International Publication Date: 12 October 1995 (12.10.95)

PCT/US95/04179

(22) International Filing Date:

3 April 1995 (03.04.95)

(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

(30) Priority Data:

08/222,664

4 April 1994 (04.04.94)

US

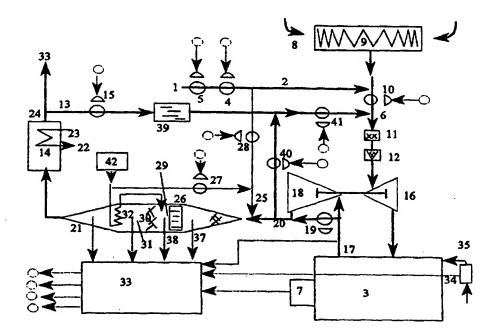
(71)(72) Applicants and Inventors: BROWN, William, Galen, II [US/US]; 720 N.W. 31st Street, Corvallis, OR 97330 (US). LOWI, Alvin, Jr. [US/US]; 2146 Toscanini Drive, San Pedro, CA 90275 (US). BENZ, Robert, Peter [US/US]; 117 Sierra Street, El Segundo, CA 90245 (US).

(74) Common Representative: BROWN, William, Galen, II; 720 N. W. 31st Street, Corvallis, OR 97330 (US).

Published

With international search report.

(54) Title: THREE-WAY CATALYTIC OXIDIZER FOR DIESEL ENGINES



(57) Abstract

A diesel engine (3) is equipped with a three-way catalytic thermal oxidizer (21), and a special manifold on the air intake to throttle and mix in air, natural gas, and cooled exhaust, to reduce nitrogen oxides emissions to extremely low levels. A computer (33) controls air flow to maintain stoichiometric fuel air ratio in the catalytic converter. Dual fueling with natural gas (1) in addition to diesel serves to reduce soot and also substitutes as a more economical fuel for the diesel it replaces. The cooled, recirculated exhaust (13) serves to reduce exhaust temperatures, reduce NO_x generation, and prevent detonation within the engine. The three-way catalytic oxidizer (21) reduces NO_x, CO, HC, and particulate emissions.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
ΑU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HÜ	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic	SD	Sudan
CG	Congo		of Korea	SE	Sweden
CH.	Switzerland	KR	Republic of Korea	SI	Slovenia
CI	Côte d'Ivoire	KZ	Kazakhstan	SK	Slovakia
CM .	Cameroon	LI	Liechtenstein	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	France	MN	Mongolia	VN	Viet Nam
GA	Gabon	••••		-	
J.A.	040011				

1

THREE-WAY CATALYTIC OXIDIZER FOR DIESEL ENGINES

TECHNICAL FIELD

The present invention relates to the operation and exhaust treatment of a diesel engine, and more particularly to a diesel engine converted to also operate on both liquid and gaseous fuel and using a three-way catalytic thermal oxidizer for exhaust treatment.

5

10

15

20

. 25

BACKGROUND ART

Diesel engines normally operate with unthrottled air intake and large amounts of excess air. All commercial diesel engines are exclusively lean-burn, intaking more air than is necessary to burn the diesel. High levels of oxygen in the exhaust from these engines necessitates the use of Selective Catalytic Reduction (SCR) for abating NOx pollutants to low levels, along with ammonia or other noxious chemicals required for SCR. Where ammonia is not used, NOx abatement is only about 50 percent effective in advanced lean-burn catalysts which use fuel in the exhaust rather than ammonia.

However, three-way catalysts have been used in automobiles in spark-ignited gasoline engines to control emissions of both nitrogen oxides, carbon monoxide (CO) and hydrocarbons (HC). The three-way catalyst is compact, highly active, inexpensive, and offers minimal resistance to the flow of exhaust while abating pollutants to extremely low levels without the need for noxious chemicals. However, no systems are presently available to effectively use three-way catalysts in diesel engines without excessive particulate emissions. The primary barrier to wider use has been inability to maintain the low oxygen levels in the engine exhaust to maintain the exact (stoichiometric) fuel air

5

10

15

20

25

30

35

2

ratio required for the three-way catalyst, without excessive sooting, and without detonation (knock) and without excessive exhaust temperatures.

Three-way catalysts offer advantage in that the single catalyst can remove both NOX, CO and HC. However, to do so requires extremely close control of the fuel air ratio both in the engine and in the catalyst, for different reasons. engine favors leaner (higher oxygen) conditions to avoid particulate emissions and combustion instability while maximum catalyst activity for reducing NOx emissions is obtained at exactly stoichiometric conditions where levels of NOx are reduced 98 percent or more depending on catalyst volume. Presence of even very slight amounts of excess oxygen can temporarily reduce catalyst effectiveness from 98 percent down to 20 percent or even lower effectiveness. Maintaining stoichiometric conditions in the catalyst bed is so critical, and such a departure from how diesel engines have ever been run, and also the basis for this invention in how it differs from prior art, that the following lengthy section is devoted to defining the conditions for effective NOx reduction in three-way catalysts as used in this invention with diesel engines.

The three-way catalyst is a catalyst which simultaneously remove the three major pollutants; hydrocarbons, However, it is only carbon monoxide, and nitrogen oxides. effective within a very narrow range of oxygen concentrations. The amount of free oxygen present in the exhaust gas is related to Redox Potential as used in scientific literature to predict the efficiency of three-way catalysts. Ford Motor Company (Hammerle SAE 810275) defines Redox Potential and shows its Redox Potential can be on catalyst performance. determined in any sample of exhaust gas using the following equation: Redox Potential = (chemical oxygen demand of the combustibles in the exhaust gas) / (oxidants actually present in the exhaust gas). So little combustibles are present in typical exhaust gas from diesel engines, that they could all be consumed

5

10

15

20

25

30

35

3

with as little as 0.01 percent by volume oxygen in the exhaust gas, whereas the exhaust gas typically contains more than 6 percent oxygen; therefore, the Redox Potential is very low in typical diesel exhaust gas at 0.01/6 or 0.002. In the preferred embodiment of the invention, the combination of means which in effect reduce the oxygen rate to the engine have never until now been commercially demonstrated in diesel engines: exhaust gas having levels of combustibles requiring 0.2 percent oxygen to consume the combustibles, and also containing about 0.2 percent actual free oxygen; this computes to a Redox Potential of 1.0. Attaining this higher exhaust gas Redox Potential is what sets this invention apart from other art for controlling emissions from diesel engines, allowing the three-way catalyst to operate highly effectively. Three-way catalysts are less than 20 percent efficient for reducing NOx in exhaust gas having a Redox Potential of less than 0.4. Whereas the catalysts may be more than 95 percent efficient at a Redox Potentials of 1.0. defined here, the "three-way catalyst" is a catalyst which is more than five times as effective in reducing NOx in exhaust gases having a Redox Potential of 1.0 than in exhaust gases having a Redox Potential of 0.3 (due to slightly higher free oxygen content). Restated, in exhaust gases having a Redox Potential of 1.0, a given volume of "three-way catalyst" will reduce NOx more effectively than five times the volume of catalyst in exhaust gases having a Redox Potential of 0.3. Zirconia or titania type oxygen sensors are known in the art to be suitable for determining Redox Potential in this application.

The preferred embodiment is featured in Figure 1 and solves a number of major problems, allowing diesel cycle engines to produce electricity on inexpensive natural gas fuel while producing virtually no pollution. Diesel cycle engines traditionally cost less than spark-ignited engines to maintain and to operate, require the least fuel input, are the most reliable machines for producing electricity. However, diesel cycle engines are also traditionally the worst offenders for NOx

5

10

15

20

25

30

4

emissions — the most serious contributor to ozone pollution. Conventional diesel engines also are not normally equipped to burn natural gas, even though natural gas can produce electricity at much lower cost since natural gas is often available at half the cost of diesel fuel. In addition, while literally thousands of large diesel engines stand—by dormant at numerous hotels and hospitals in this country, diesel fuel costs and air pollution levels are too high to allow these engines to produce inexpensive electricity and heat.

Thermal oxidizers of reasonably small size must operate at high temperatures higher than 1300 F in order to combustible particulates primarily carbon. However long engine life requires exhaust temperatures lower than 1175 F. But the effectiveness of thermal oxidizers is very sensitive to temperature. Oxidizing particulates at 1175 F versus 1300 F exhaust temperature requires a thermal oxidizer at least five times larger possibly exceeding the volume of the whole engine.

DISCLOSURE OF THE INVENTION

A diesel engine is equipped with a three-way catalytic thermal oxidizer, and a special manifold on the air intake to throttle and mix in air, natural gas, and cooled exhaust, to reduce nitrogen oxides emissions to extremely low levels. A computer controls air flow to maintain stoichiometric fuel air ratio in the catalytic converter. Dual fueling with natural gas serves to reduce soot and also substitutes as a more economical fuel for the diesel it replaces. The cooled, recirculated exhaust serves to reduce exhaust temperatures, reduce NOx generation, and prevent detonation within the engine. The three-way catalytic oxidizer reduces NOx, CO, HC, and particulate emissions. This invention relates to control of diesel engines to reduce emissions including NOx, including thermally oxidizing particulates and dual fueling with natural gas to maintain

5

10

15

20

25

30

35

5

stoichiometric conditions in a three-way catalyst in the exhaust stream.

A computer controls combustion air flow to maintain stoichiometric fuel air ratio in the catalytic converter. fueling with natural gas serves to reduce soot and substitutes as a more economical fuel for the diesel it replaces. The cooled, recirculated exhaust serves at least three purposes: to prevent autoignition (knock) within the engine, reduce exhaust temperatures, and reduce NOx generation. Natural gas is also injected into the exhaust stream just upstream of the catalyst to allow the catalyst to effectively operate in exhaust gases containing 1 or 2 percent oxygen, so that the engine can operate with a very slightly leaner mixture and not be so subject to sooting, and also be easier to control. The system maintains moderately high exhaust temperatures over a wide load range which ensures excellent catalyst activity. Low sulfur fuels are used to extend the operating range and life of the catalyst.

The preferred embodiment of this invention allows existing diesel engines to be retrofitted to operate primarily on natural gas while reducing emissions to near zero levels. At the same time operation is not compromised at full load on straight diesel fuel.

This invention reduces particulates by a thermal oxidizer and restricts the flow of fresh air into the diesel engine, by throttling and other means, to admit just enough air to oxidize the fuel and little more. This is a major departure from the operation of conventional diesel engines which normally operate with at least 50 percent more air than is needed to oxidize the fuel, and often with up to 1000 percent more air than is needed to oxidize the fuel at light loads. NOx emissions at the catalyst outlet rise dramatically twenty-fold or more when even tiny amounts of excess air are admitted into the engine intake. It is not obvious to throttle the intake to a diesel engine to operate the engine with extremely low levels of oxygen in the exhaust gas. Without the features of the present invention which

10

15

20

25

30

35

DAIGDOOLD 1400 050710041 1 -

include recirculating cooled exhaust gas into the intake of the engine, exhaust gas temperatures may rise to 1800 degrees F, destroying or requiring major redesign of key components of the engine including the turbocharger and the fuel injector tips in the cylinders of the engine. And without providing natural gas into the intake of the engine, the engine may also run roughly, and inefficiently, smoking heavily while its air intake is restricted. Such heavy smoke is harmful to operation fouling oil and contributing to engine wear regardless of after treatment of exhaust gases.

As mentioned, the primary feature of the present invention is to operate the diesel engine with a thermal oxidizer with throttled air intake and other means to restrict oxygen intake so that the exhaust entering the catalyst has a high Redox Potential. While conventional diesel engines seldom operate at Redox Potentials exceeding 0.01, the invention attains Redox Potentials of from 0.5 to 2 in the diesel exhaust in the catalyst bed. The high Redox Potential is used in combination with a three-way catalyst to simultaneously remove the three major pollutants, NOx, HC and CO. Other features of the present invention, including recirculation of cooled exhaust gas into the engine which prevents knock and cools the exhaust, make the invention feasible for existing diesel engines, at very low cost of retrofit.

The invention makes it possible, for the first time known, to retrofit existing diesel engines to generate electricity using inexpensive natural gas fuel while producing minimal levels of pollution. This is extremely significant because there are numerous back up generators at hotels which are now available to generate inexpensive electricity and heat if lower cost natural gas can be burned rather than diesel, and if exhaust emissions can be reduced from the extreme levels associated with diesel engines. Normally these engines operate with large amounts of excess air. However, by allowing such engines to burn fuel nearly stoichiometrically, three-way catalysts may be used

5

10

15

20

25

35

7

economically. Thus this invention provides an inexpensive means for retrofitting such engines to primarily burn natural gas to generate electricity while producing less pollution than utility power plants per kilowatthour generated.

It is therefore an object of the invention to effectively utilize the three way catalyst to produce very low emissions of NOX and particulate, and also of CO and HC. Yet another object is to provide immediate full-load operation on straight diesel during curtailment of gas fuel. Still another object is to provide a catalytic control system which allows less strict control of the air-fuel ratio. Yet another object is to limit catalyst temperatures in order to sustain reasonable catalyst activities over a long life of the catalyst. Yet another object is to use readily available, inexpensive transducers and controls to maintain operation of the catalyst system. Still another object is to control combustion air flow rate quickly, to follow a rapidly changing flow of fuel while maintaining close tolerances on the fuel-air ratio. Yet another object is to reduce formation of particulate. Still another object is to prevent fouling of the catalyst and exhaust gas heat exchanger, and to control those particulate which are emitted from the engine by maintaining reasonably high temperatures and at least partially oxidizing conditions. Yet another object is to prevent excessive exhaust temperatures and detonation (knock) within the diesel engine. Still another object is to operate a diesel engine over a wide load range while maintaining the catalyst bed at a stoichiometric fuel air ratio. Yet another object is to effectively control the gas and liquid flow to the engine to obtain efficient combustion while minimizing fuel costs. another object is to effectively utilize a wide range of fuels as an energy source for the engine, including gases which contain propane. Yet another object is to reduce the number of automatic control valves needed to operate the system. Still another object is to provide an engine control system which can easily be retrofit to existing engines, including stand-by generators.

8

Yet another object is to be able to recover waste heat from the engine exhaust for use in cogeneration applications. Still another object is prevent ignition delay in the engine, so that the engine continues to run efficiently and maintains relatively low exhaust temperatures. Still another object is to throttle engine intake air only to minimal vacuum conditions. Yet another object is to reduce the ash, sulfur and other contaminants in the engine exhaust so that the life of the catalyst is extended. Still another object applies when the gas contains sulfur in significant amounts, to operate the catalyst at high temperatures to preserve the activity of the catalyst. Yet another object is to prevent corrosive constituents of gases from entering the engine.

BRIEF DESCRIPTION OF THE DRAWINGS

15

5

10

FIG. 1 is a diagrammatic depiction of an emission control system suitable for diesel engines.

BEST MODE OF CARRYING OUT THE INVENTION

FIG. 1 is a diagrammatic depiction of the preferred embodiment Natural gas 1 at 30 psig is served through 20 of the invention. a 1 1/4" diameter pipeline 2 to a retrofit Caterpillar Model 3412 diesel engine 3. Low pressure natural gas is also suitable since the engine draws in gas in partial vacuum conditions. Flow of natural gas to the engine is controlled through a one inch control valve 4. An additional shut off valve 5 cuts off gas in 25 the event of a control failure. Natural gas is drawn into the air intake 6 to displace diesel as fuel. The existing governor 7 on the engine senses an increase in power, and cuts back the diesel flow due to natural gas burning along with the diesel within the cylinders. Combustion air 8 is also drawn into the 30 intake; first through in-line filter 9, then through a primary

throttling valve 10, and finally through the static mixer 11. The static mixer is one such as is commonly available from KOCH Engineering for mixing fluids in line through a pipe. A conical screen 12 may also be included to provide micromixing which is advantageous to uniform combustion in the cylinders. The screen 5 12 typically is 16 mesh with 0.015 inch diameter wires. Cool EGR 13 from the outlet of the heat recovery heat exchanger 14 is ducted through the EGR control valve 15 and also provided to the static mixer 11. The gases advance from the static mixer to the 10 turbocharger compressor 16 (if the engine is equipped with a turbo), in which case engine exhaust 17 flows through the turbocharger turbine 18. Where practical the waste gate valve 19 may also be used to bypass exhaust around the turbine to reduce exhaust back pressure while also decreasing air inlet 15 pressure to the engine, to improve efficiency and reduce the throttling needed across the valve 10. Note that the invention is also effective on engines without turbocharging. Untreated exhaust gases 20 pass to the combined 3-way catalytic oxidizer 21 and is purified. Heat is recovered from the purified exhaust 20 in the heat recovery unit 14 producing steam 22 from feedwater 23 for process use. Exhaust 24 exits from the heat recovery heat exchanger 14 at about 450 degrees F. Fuel 25 may be injected upstream of the catalyst to produce near stoichiometric conditions in the main catalyst 26. Use of fuel 25 offers the 25 additional advantage of allowing the engine to operate slightly lean with exhaust oxygen levels ranging from 0.5 to 3 percent, preferably about 1%. Higher exhaust oxygen levels allow the engine to operate closer to the conditions for which it was originally designed, and results in lower particulate emissions. 30 However, in conditions requiring greater resistance to knock and where more soot in the engine may be tolerated, the engine may also be run fuel rich, with the blower 42 injecting air ahead of the catalyst through the valve 27 rather than fuel being injected through the valve 28. The exhaust oxygen combines with the fuel 25 in the main catalyst 26, creating a temperature rise through 35 ·

the catalyst of about 75 to 300 degrees F and leaving the exhaust stream 29 depleted of free oxygen. Exhaust oxygen is replenished as the blower 42 blows air at a flowrate of 5 to 10% of the exhaust flow. Mixer 30 thoroughly mixes the air with the exhaust which proceeds through the oxidation chamber 31. A coil 32 preheats the blower air to keep the exhaust mixer 30 and chamber 31 as hot as possible, without requiring excessive catalyst 26 temperatures. After recovering heat from the purified exhaust, the exhaust is vented 33.

10 Control is as follows. During start up the engine operates normally at up to full load on straight diesel, with the gas valve 5 shut off, the EGR valve 15 closed, and the inlet air throttle 10 fully open. Then computer controller 33 opens the gas valves to increase gas flow until the engine begins to use only about 10 to 20 percent of its full load diesel fuel flow. The existing governor 7 on the engine senses an increase in power, and cuts back the diesel flow due to ignition of natural gas along with diesel within the cylinders. Diesel fuel flow may be monitored by a number of methods:

- A) By reading the governor 7 current signal 29 and controlling gas to achieve a value typical of 10% load on diesel only;

 B) By reading the droop in frequency of the generator, perhaps of 0.5 Hz to maintain an actual operating frequency of perhaps 59.5 Hz.
- C) By reading net diesel 34 flow into the engine through the flowmeter 35

 Finally the computer opens the EGR valve 15 and fuel injector valve 28 to add fuel equivalent in heating value to about one half percent methane by volume of the exhaust, and gradually closes the throttle 10 until the signal from the exhaust oxygen sensor 37 approaches the stoichiometric signal level. The fuel injected through the valve 28 maintains the catalyst at stoichiometric conditions while allowing the engine to operate
- 35 1 percent excess oxygen in the cylinders reduces sooting,

with approximately 1 percent oxygen levels in the exhaust.

eliminates the need for particulate traps (as shown in Figure 2) in the exhaust line, and also improves control of the engine since the oxygen is available to burn additional diesel on suddenly increasing load demands seen by the engine. Without the extra oxygen, sudden increases in injected diesel results in reduced power from the engine, bogging down the engine and producing heavy smoke. An additional oxygen sensor 38 may also be helpful in controlling air-fuel ratio in engine exhaust.

Normal diesels operate with their exhaust gases containing from 35 to 1000 percent excess air over their load range from full load to no load. In the preferred embodiment, the dual fuel natural gas/ diesel engine operates at from 120 percent of full load down to 35 percent of full load at stoichiometric conditions without smoke. Exhaust temperatures are maintained at from 1000 to 1250 degrees F by recirculating cooled exhaust gas into the air intake. The exhaust temperatures are ideal for high catalyst activity and long catalyst life. In addition this exhaust gas recirculation (EGR) prevents knocking or detonation or autoignition of the gases within the cylinders, prolonging engine life. At heavy loads, EGR flows are typically 20 percent of the exhaust mass flow through the engine exhaust manifold; typically 35 percent at light loads.

The recirculated exhaust is treated through the absorber 39 to remove sulfur acids potentially harmful to the engine 3. engine 51. The contents of the absorber 39 may be as simple as an alumina coated ceramic honeycomb, periodically replaced or regenerated by exposure to exhaust at above 900 degrees F. The absorber 39 may also be a particulate trap suitably coated with alumina as is common art for honeycomb catalysts. Regeneration may be accomplished by periodically running the hot engine exhaust through a diverter valve 40 while the EGR valve 41 is closed. In addition, this regeneration process serves to back flush the absorber 39, burn off soot, while heating the alumina to sufficiently high temperatures to drive off sulfuric acid. In most cases, use of low-sulfur fuels should eliminate the need



for the absorber 39.

It will be understood that various changes may be made in the invention without departing from the following claims. Therefore the scope of the invention should only be limited by the following claims.

ران المتعابد المحادث

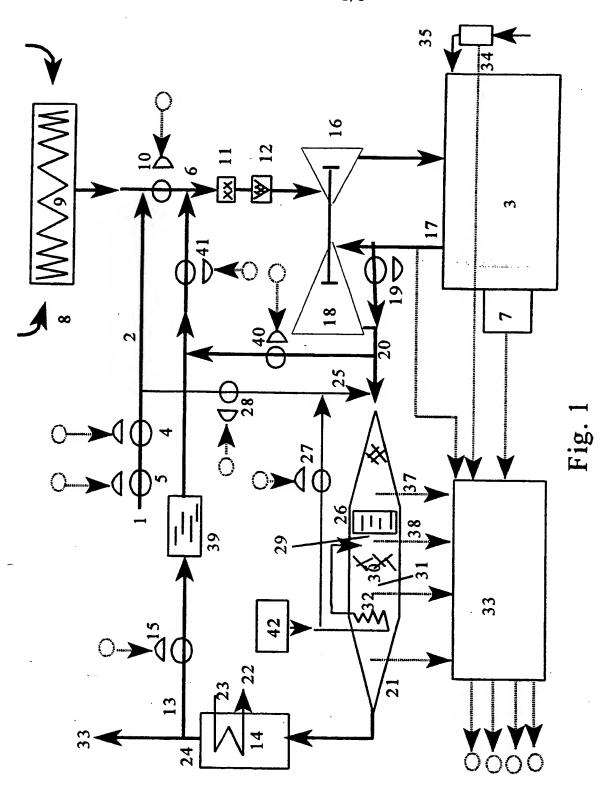
WHAT IS CLAIMED IS:

- 1 1. A process for producing power with minimal emissions of
- 2 pollutants comprising:
- 3 feeding a mixture comprising air and natural gas into the intake
- 4 of a diesel engine;
- 5 igniting said gaseous fuel by injecting liquid fuel into said
- 6 engine to produce power and exhaust gases with less than 3
- 7 percent oxygen content;
- 8 passing said exhaust gases at a redox potential of 0.5 to 1.5
- 9 through a main catalyst bed to remove at least 50 percent of the
- 10 nitrogen oxides from said exhaust gases to produce low-NOx
- 11 exhaust gases;
- adding at least 5% by weight air to said low-NOx exhaust gases
- and passing said oxygenated exhaust gases through a thermal
- oxidizer to remove at least 50% of the combustible particulates
- 15 from said exhaust gases.
- 16 2. The process according to claim 1 wherein said mixture has
- 17 less than 19 percent oxygen by volume.
- 18 3. The process according to claim 2 wherein said mixture
- comprises at least 10 percent by weight of said exhaust gases to
- 20 reduce knock within said engine.
- 21 4. The process according to claim 3 wherein said exhaust gases
- 22 are cooled to a temperature of less than 300 F prior to mixing
- 23 into said mixture to further reduce knock within said engine and
- 24 to reduce exhaust temperature.

25 5. The process according to claim 4 wherein said cooled exhaust

- 1 gas is conditioned through an acid absorbing bed to remove
- 2 sulfuric acid from said exhaust gas prior to introducing said
- 3 exhaust gas into said engine.
- 4 6. The process according to claim 1 including the step of adding
- 5 additional fuel to said exhaust gases prior to introducing said
- 6 gases into said main catalyst bed to achieve the required redox
- 7 potential of 0.5 to 1.5 to achieve effective catalyst activity.
- 8 7. The process according to claim 1 including the step of
- 9 controlling the oxygen level in said exhaust by bypassing at
- least a portion of said exhaust from said engine through a waste
- gate to reduce the boost pressure of said engine and reduce the
- 12 oxygen level in said exhaust.
 - 8. The process according to claim 3 wherein said mixture is passed through a screen to promote micromixing of said mixture for improved combustion within said engine.

BRIGOCCIDE AND DESTROBAT I



SUBSTITUTE SHEET (RULE 26)

A. CLASSIFICATION OF SUBJECT MATTER							
IPC(6) :	Please See Extra Sheet.	213.7. 215.5					
US CL :60:274, 278, 298, 303, 602, 605.2: 423:212c, 213.2, 213.7, 215.5 According to International Patent Classification (IPC) or to both national classification and IPC							
	DS SEARCHED						
Minimum de	ocumentation searched (classification system followed l	ny classification symbols)					
	U.S. : 60:274, 278, 298, 303, 602, 605.2; 423:212e, 213.2, 213.7, 215.5, 239.1						
Documentat	ion searched other than minimum documentation to the c	extent that such documents are included	in the fields searched				
NONE							
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) NONE							
C. DOC	UMENTS CONSIDERED TO BE RELEVANT						
Category*	Citation of document, with indication, where app	ropriate, of the relevant passages	Relevant to claim No.				
Υ	JP,A, 3-94,817 (Nippon Shokubai English abstract.	Kagaku) 19 April 1991,	1-8				
Y	JP,A, 54-23,825 (Toyota) 22 February 1979, English 1,3,4 abstract.						
Y	US,A, 4,955,326 (Helmich) 11 September 1990, col. 4, lines 24-33, claims 1-3.						
Y	US,A, 4,445,488 (Tanaka et al) 01 May 1984, col 6, lines 1- 7 15.						
Y	US,A, 3,739,583 (Tourtellotte et al) 19 June 1973, col. 2 2,3 lines 8-23.						
X Furt	her documents are listed in the continuation of Box C.						
1	 Special categories of cited documents: T^{**} later document published after the international filing date or priorit date and mu in conflict with the application but cited to understand the 						
"A" do	ocument defining the general state of the art which is not considered to be of particular relevance.	"X" document of particular relevance; to					
4	artier document published on or after the international filing date	"X" document of particular relevance; (considered novel or cannot be considered novel or cannot be considered novel or cannot be considered.	lered to involve an inventive step				
ci	ocument which may throw doubts on priority claim(s) or which is ited to establish the publication date of another citation or other	"Y" document of particular relevance;	the claimed invention cannot be				
.O. q	pecial reason (as specified) ocument referring to an oral disclosure, use, exhibition or other neura	considered to involve an inventive combined with one or more other su- being obvious to a person skilled in	c step when the document is ich documents, such combination				
•P• d	ocument published prior to the international filing date but fater than the priority date claimed	"X" document member of the same pate	nt family				
Date of the actual completion of the international search Date of mailing of the international search			earch report				
12 MAY 1995 15 JUN 1995							
Box PCT	mailing address of the ISA/US ioner of Patents and Trademarks on, D.C. 20231	Authorized office and a second of the second	level,				
Facsimile No. (703) 305-3230		Telephone No. (703) 308-2540					

		101/03/3/041	
C (Continua	ntion). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the releva	int passages	Relevant to claim N
Y	US, A, 3,909,449 (Nagai et al.) 30 September 1975, col 39-49	. 5, lines	5
· .	US, A, 3,826,810 (Lawson) 30 July 1974, col. 2, lines :	59-65	4
,	US,A, 4,712,643 (Iles et al.) 15 December 1987, col. 1 14 and col. 2 lines 62-66.	, lines 5-	1
A,P	US, A, 5,357,749 (Ohsuga et al.) 25 October 1994, claims 1-25		
.,P	US,A, 5,354,544 (Logan et al) 11 October 1994, claims 1-9. 1-8		1-8
	•		
	•		
	• •		
		·	
			•
	•	ļ	
		[.	

Form PCT/ISA/210 (continuation of second sheet)(July 1992)*

A. CLASSIFICATION OF SUBJECT MATTER: IPC (6):						
F0IN: 3/00, 310; F02D 23/00; B01D 49/00: 53/92, 53/94; C01B 21/20						
*						
	د د دعست ۱					
	-					
	,					

Form PCT/ISA/210 (extra sheet)(July 1992)*